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**WO 02/05294 A1**

(54) Title: **ELECTRICALLY CONDUCTIVE INK**

(57) Abstract: The invention relates to the use of electrically conductive inks, said inks comprising electrically conductive powder and electrically conducting fibres, wherein the aspect ratio of the fibres is greater than 2:1. The inks are used to form electrically conductive layers, especially in optoelectronic devices such as solar cells. The layers have considerably reduced electrical resistance than if the electrically conductive powder were used alone.

## ELECTRICALLY CONDUCTIVE INK

The present invention relates to the use of conductive inks to form electrically conductive layers, especially in optoelectronic devices.

In any form of electrical power generation device, power conversion losses due to ohmic resistance of internal conductive pathways is usually undesirable and must be kept to a minimum. In conventional solid-state solar cells that convert light energy into electrical energy, such as those based on silicon, printed tracks made e.g. from silver pastes are commonly used to carry the electrical current from the active part of the cell to the external environment. Silver or similar metals are used due to their low electrical resistance. Newer types of solar cells incorporating e.g. solid polymer electrolytes and/or dye-sensitised semi-conductor powders may or may not be able to use conducting tracks based on metal pastes depending upon the chemical environment within the cells and also upon cost considerations. There is therefore a need to develop alternative conducting track and/or electrode materials for use in these types of cells that are more chemically resistant and/or are cheaper.

Particulate materials, such as e.g. carbon, are well-established electrical conductors that have been used as track and electrode material in solar cells. WO 94/15344 discloses a conductive ink comprising carbon particulate materials. Particulate carbon has also been used as part of the counter-electrode in dye-sensitised solar cells (so called Graetzel cells), often applied to substrates in the form of a paste or as an ink. However, electrical conductivity in the carbon layer or film produced under these circumstances relies on point-to-point contact between small, frequently micro-sized, carbon particles. Thus the electrical pathway is both tortuous and very sensitive to the physical and chemical nature of the carbon particle surfaces.

It has now been found that if such particulate conductive materials, such as e.g. carbon, are partially replaced by conductive fibres in inks, the resultant conductive inks or layers produced therefrom are significantly more conductive than an equivalent volume of particulate materials.

Thus, in the first aspect the present invention provides for the use of an electrically conductive ink comprising an electrically conductive powder and electrically conductive fibres wherein the aspect ratio of the fibres is greater than 2:1, to form an electrically conductive layer.

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The electrically conductive powder suitably comprises one or more conductive particulate materials such as carbon, nickel, tungsten and F-doped tin oxide, but is preferably carbon powder. Specific examples of carbon powder that can be used include, but are not limited to, Vulcan XC72R (Cabot Carbon Limited, Stanlow, Ellesmere Port, South Wirral, L65 4HT, UK) and TIMREX KS15 Graphite (Timcal Ltd, CH-6743, Bodio, Switzerland). The electrically conductive powder suitably has a surface area in the range from 5 to 1000m<sup>2</sup>/g, preferably from 20 to 250m<sup>2</sup>/g.

The electrically conductive fibres have an aspect ratio of greater than 2:1, preferably greater than 10:1. The fibres may be any electrically conductive fibres, including carbon, nickel, tungsten and F-doped tin oxide, but are preferably carbon fibres. The fibres must be chosen to ensure that they are chemically compatible with the other components. The fibres are suitably of a length of at least 1 micron, preferably greater than 1mm. The conducting fibres preferably have a thickness of not more than 100 microns, preferably not more than 50 microns. Specific examples of conductive carbon fibres that may be used in the compositions of the present invention include, but are not limited to, Toray M40B 6000 50B (Toray Industries, Japan) and Graphil 34-700 12 K (Grafil Europe, Sutherland House, Matlock Road, Coventry, CV1 4JQ, UK).

The relative ratio by weight of fibres to powder is suitably in the range from 10E-04 to 1, preferably from 0.01 to 0.5.

The electrically conductive layer may be a film, an electrode or an electrically conductive track. There may be a preferred orientation of the electrically conductive fibres within the layer because this may enhance conductivity in a particular direction. For example, the ink may be used to form a track wherein the majority of the fibres are oriented along the direction of the track. It is possible that this will increase conductivity in the direction of the track.

The component fibres and powders may be mixed together using the following technique. An ink is made-up by hand, eg using the proportions 28.4wt% carbon powder, 17% Disperbyk 164 surfactant (Byk, Holland) and 54.6% pine oil, followed by triple-roll milling to ensure even mixing. This 'base' ink typically has a viscosity of approximately 100 Pa. The desired weight of fibre, pre-cut to the required length, is added to the base ink with manual stirring or for instance using a paddle-stirrer. After stirring for several minutes to ensure adequate mixing, the ink is ready for use. Such mixtures are suitably converted into films or tracks by applying the mixture to a substrate surface, preferably a smooth surface, by e.g. screen-printing or some similar technique and allowing the same to dry followed by suitable firing in an air or nitrogen atmosphere between 300-500°C.

The ink used in the present invention is particularly useful for making electrodes in optoelectronic devices such as solar cells (including photovoltaic cells). For instance in a solar cell, such electrodes are used for the purpose of transporting the electrical current generated by the photo-active components away to an external circuit or the next cell in a series or parallel configuration etc. The film may also serve to protect the internals of the cell from the external environment.

In a second aspect the present invention provides a solar cell comprising an electrically conductive layer formed by the use of an electrically conductive ink according to the present invention.

In a final aspect, the present invention provides a photovoltaic cell comprising an electrically conductive layer formed by the use of an electrically conductive ink according to the present invention.

The present invention is illustrated with reference to the following Example:

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#### EXAMPLE 1

Carbon fibres, of length 1 mm were mixed in with a 'base' carbon powder ink made as described hereinbefore, by continuously stirring with a spatula for 5 minutes.

The weight ratio of carbon fibre to ink was 1:3. The fibre-containing ink was then used to form thin films of 1 x 5cm dimension on float glass substrates by screen-printing through a nylon mesh of 150 holes per inch. A single or double-pass print was normally sufficient to produce a coherent strip approximately 100 microns thick before drying.

- 5 After printing of the film, the piece was fired in an air oven at 450°C for 16 minutes in air.

The conductivity of the film was measured using a standard '4-point probe' technique using a Jandel scientific commercial instrument. This technique is widely  
10 used in industry for measuring electrical conductivities. Test samples were prepared as 1 x 5cm strips on clear float glass substrates as described previously. Electrical contact was made either end of the longer side by coating silver-paint (Agar Scientific) overlays onto the samples with an overlap of 2mm each end. One current-driving and one potential-sensing lead were then connected to each end of the strip and the conductivity  
15 read directly on a Hewlett Packard high-impedance systems meter. All tests were done at room temperature and humidity. The results of this test are shown in Table 1 below:

**TABLE 1**

Sample tested	Thickness of 1 x 5 cm strip (microns)	Resistance across length of strip (kilo-ohms)
Carbon particulate layer ink	30-40	25.8
As above but with added fibres	30-40	0.47

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These results show that the combination of a carbon powder ink with carbon fibres results in a considerable reduction in the resistance of the resultant product.

**CLAIMS**

1. The use of an electrically conductive ink comprising an electrically conductive powder and electrically conductive fibres wherein the aspect ratio of the fibres is greater  
5 than 2:1, to form an electrically conductive layer.
2. The use of an electrically conductive ink as claimed in claim 1 wherein the electrically conductive powder comprises one or more of carbon, nickel, tungsten and F-doped tin oxide.  
10
3. The use of an electrically conductive ink as claimed in claim 1 wherein the electrically conductive powder is carbon powder.
4. The use of an electrically conductive ink as claimed in any one preceding claims  
15 wherein the electrically conductive powder has a surface area in the range from 5 to 1000 m<sup>2</sup>/g.
5. The use of an electrically conductive ink as claimed any one of the preceding claims wherein the electrically conducting fibres are selected from carbon, nickel,  
20 tungsten and F-doped tin oxide.
6. The use of an electrically conductive ink as claimed in claim 5 wherein the electrically conducting fibres are carbon fibres.
- 25 7. The use of an electrically conductive ink as claimed in any one of the preceding claims wherein the electrically conductive fibres have a length of at least 1 micron.
8. The use of an electrically conductive ink as claimed in any one preceding claims wherein the electrically conductive fibres have a thickness of not more than 100 microns.  
30
9. The use of an electrically conductive ink as claimed in any one of the preceding claims wherein the relative ratio by weight of electrically conductive fibres to electrically conductive powder is in the range from 10E-04 to 1.

10. A solar cell comprising an electrically conductive layer formed by the use of an electrically conductive ink as claimed in any one of the preceding claims.

11. A photovoltaic cell comprising an electrically conductive layer formed by the use  
5 of an electrically conductive ink as claimed in any of claims 1-9.

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<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC 7	H01B1/22 H01L51/20	H01B1/24 C09D11/00 H01G9/20 F03G6/00
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
IPC 7 H01B C09D H01G F03G H01L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
EPO-Internal, WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
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